4. OPERATIONAL PLAN FOR PHASE II

The Phase I air quality data analysis and results of other investigations lead to several alternative hypotheses for the WE effect. This section describes these hypotheses and the data analysis approach and measurement plan for Phase II to address these hypotheses. Because of resource limitations and time constraints, the proposed experimental design focuses on short-term investigations of emissions-related hypotheses. The investigation of meteorological influences of the WE effect requires much longer term investigations than allowed by the current scope of Phase II. These factors will be addressed in Phase III utilizing supplemental data sources, which include historic SCAQMD monitoring data, recent PAMS hydrocarbon data, and relevant data from recent field studies such as the 1997 Southern California Ozone Study (SCOS-NARSTO) and the Central California Ozone Study (CCOS).

4.1 Hypotheses for the Weekend Ozone Effect

The hypotheses for the day-of-week differences in ozone consist of a set of hypothetical effects related to air quality, photochemistry, meteorology, and emissions. One subset of hypotheses is related to the interactions of ambient concentrations of VOC and NOx, chemical transformations, and transport that affect the day-of-the-week differences in the diurnal evolution of ozone chemistry. The second subset hypothesizes emission-activity differences between weekdays and weekends that affect the photochemistry so that changes in emissions could explain day-of-the-week differences in observed ambient concentrations of NOx, VOC, and VOC/NOx ratios.

There are seven hypotheses related to air quality that are categorized into three types. The first type is related to changes in O_3 inhibition, the second type is related to ozone formation rates, and the third type is related to day-of-the-week differences in photolysis rates. Under each of the seven air quality hypotheses, emission hypotheses that are the presumed cause of the air quality effect are identified (by small letters).

A. Changes in O_3 inhibition on weekends.

1. Lower NO concentrations on weekend mornings result in decreased ozone inhibition than on weekday mornings.

    a. Heavy-duty diesel truck (and bus, train) activity is less on weekends during the ozone inhibition period than on weekdays resulting in lower NO concentrations and less ozone inhibition.

    b. On-road light-duty gasoline vehicular activity is less on weekends during the ozone inhibition period than on weekdays resulting in lower NO concentrations and less ozone inhibition.

B. Changes in ozone formation rates due to changes in VOC/NOx ratio or other factors.

2. Lower NO concentrations on weekend mornings result in higher VOC/NOx ratios than on weekday mornings.

    a. Heavy-duty diesel truck (and bus, train) activity is less on weekends during the ozone accumulation period than on weekdays resulting in higher VOC/NOx ratios and higher ozone formation rates.

    b. On-road light-duty gasoline vehicular activity on weekends is similar or higher than weekdays during the ozone accumulation period. Lower diesel NOx emissions during the same period results in higher weekend VOC/NOx ratios during this period.

3. Higher VOC concentrations on weekends result in higher VOC/NOx ratios than on weekday mornings.

    a. Use of off-road recreational vehicles, lawn and garden equipment, backyard barbecues, and household solvents are increased on weekends compared to weekdays resulting in higher weekend VOC/NOx ratios.

4. Greater carryover of VOC concentrations relative to NOx on Friday and Saturday evenings results in higher VOC/NOx ratios and increased rate of ozone formation on Saturday and Sunday mornings.

    a. Heavy-duty diesel activity is decreased on Friday and Saturday evenings compared to other evenings resulting in overnight carry over of pollutants with higher VOC/NOx ratios.

    b. Light-duty gasoline vehicle traffic is increased while heavy-duty diesel traffic is decreased on Friday and Saturday evenings compared to other evenings resulting in overnight carry over of pollutants with higher VOC/NOx ratios.

5. Greater contribution of aloft VOC to surface VOC concentrations on weekends during the ozone accumulation period increases the rate of ozone formation compared to weekdays.

6. Because O_3 inhibition is lower on weekends, HONO, HCHO, PAN, or other early-morning radical sources increase in relative importance. These radical sources may be contained in the surface or aloft carryover.

C. Higher photolysis rates on weekends

7. Lower PM concentrations during weekends increases the direct and scattered UV available for photolysis, thus increasing the rate of ozone formation compared to weekdays.

    a. Lower vehicle traffic on weekends, especially heavy-duty diesel truck (and bus, train), results in lower direct emissions of soot particles that absorb light.

b. Lower vehicle traffic on weekends, especially heavy-duty diesel truck (and bus, train), results in lower emissions of NOx that reacts to form secondary nitrate particles.

4.2 Phase II Measurement Plan

The proposed experimental design for the Phase II field study focuses on short-term investigations of emissions-related hypotheses. DRI will conduct more detailed time-resolved measurements to test the hypothesized relationship between emissions sources and the diurnal and day-of-the-week variations in CO, NO, NOx, VOC, VOC/NOx and NO_2/NOx. The field study measurements focus on attribution of ambient precursor concentrations to major sources of VOC and NOx. The measurements involve two approaches: supplemental measurements at existing SCAQMD monitoring sites and mobile sampling during periods that coincide with overnight carryover of O_3 precursors, O_3 inhibition, and O_3 accumulation. STI will gather and compile existing and new emissions data that will support testing of weekend/weekday emissions hypotheses as described above (Roberts et al., 2000).

4.2.1 Supplemental Measurements at SCAQMD Monitoring Stations

Supplemental measurements by DRI at the monitoring stations include hourly C_2 to C_{11} volatile organic compounds by automated gas chromatography with ion-trap mass spectrometry at Azusa, continuous black carbon by light absorption with an aethalometer (approximately 5-minute averages) at Azusa and Pico Rivera, and 3-hour composite Tenax samples for C_8 to C_{18} hydrocarbons beginning at 0200, 0600, and 0900 PDT on 9/30, 10/1, 10/2, 10/4, 10/6, 10/7, and 10/8. ARB will collect canister samples at Los Angeles – N. Main for speciated hydrocarbons on the same schedule, and SCAQMD will measure 3-hour average speciated VOC with an automated gas chromatograph at Pico Rivera. The analysis of the data in Phase III of the study will also take advantage of the CO and NOx measurements from the SCAQMD's monitoring network shown in Table 4-1.

4.2.2 Mobile Monitoring

Primary pollutants (CO, NO, black carbon [BC] and speciated hydrocarbons) will be measured simultaneously in a mobile van along several freeway loops in different areas of the basin. Carbon monoxide (TEI 48), NO/NOy (TEI 42S) and black carbon estimated from light absorption (Anderson RTAA-1000 aethalometer) will be measured continuously with averaging times of 1, 1, and 5 minutes, respectively. Integrated canister and Tenax cartridge samples will be collected over a period of approximately 50 minutes during each freeway loop and at fixed locations. Sonoma Technology, Inc. will conduct concurrent traffic and emission source surveys during the field study.

Mobile sampling will be conducted during the carryover period between 2-5 a.m. (PDT), the ozone inhibition period between 6 to 9 a.m., and during the ozone accumulation period between 9 a.m. and noon. Measurements will be made on Saturday (9/30), Sunday (10/1), Monday (10/2), Wednesday (10/4), Friday (10/6), Saturday (10/7), and Sunday (10/8) along the following loops and fixed locations.

- 0200 to 0245 - Industry Hills Conference Center (overflow parking lot on the south end of the conference center) on all days.

- 0300 to 0345 - Covina Loop (east on S-60 from Azusa Avenue onramp, north on S-57, west on I-10 to I-5) on all days.

- 0415 to 0500 – Dodger Stadium (four loops around the perimeter of the Stadium) on all days.

- 0515 to 0600 – Compton Loop (south on S-110 from Stadium Way onramp, east on I-405, north on I-710 to I-10) on all days.

- 0630 to 0715 – Source-dominated samples for SI vehicle exhaust profile (fixed location sampling on southbound S-110 just south of Stadium Way onramp) on 10/2, 10/4, 10/6, 10/7 and 10/8. The Pasadena Freeway is restricted to automotive traffic only.

- 0730 to 0815 – Dodger Stadium on all days.

- 0830 to 0915 – Compton Loop on all days.

- 0930 to 1015 - Covina Loop (east on I-10 at I-710, south on S-57, west on S-60 to Azusa Avenue offramp) on all days.

- 1030 to 1115 - Industry Hills Conference Center on all days.

- 1130 to 1215 - Pomona Loop (east on S-60 at Azusa Blvd onramp, north on I-15, west on I-10, north on 210 to Azusa Avenue offramp on 10/2, 10/4, 10/6, 107, and 10/8.

Five sets of canister and Tenax samples and continuous CO, NO, NOy and black carbon measurements will also be taken at a truck stop near I-10 and I-15. Measurements will be made during the early morning hours from 0100 to 0500, and will consist of three sets of samples at the truck stop and upwind samples before and after the truck stop samples. Additionally, ten gasoline and two diesel fuel samples will be collected for analysis of speciated VOCs. The canister samples will be analyzed in the laboratory for CO, CO_2, methane, MTBE, and C_2-C_{11} hydrocarbons, and C_8-C_{18} hydrocarbons will be quantified from Tenax samples.

4.2.3 Measurement Methods

This section describes the methods that will be used to carry out the measurements that are proposed in Sections 4.2.1 and 4.2.2.

Aethalometer

Light absorbing aerosol (e.g., black carbon) deposited on a filter can be quantified through the measurement of light transmission or reflection. A real-time version of the integrating plate method, the aethalometer, continuously collects aerosol on a quartz-fiber filter tape. During the deposition process, the light attenuation through the aerosol collection spot and an unloaded reference spot are monitored. Their difference yields the absorption due to the integral of all light-absorbing materials collected on a particular spot. The time derivative of this

quantity is a measure of the current aerosol light absorption. When the optical density of the aerosol spot reaches a certain value, the filter tape advances automatically. Time resolution available with the aethalometer varies from seconds or minutes in urban areas to ten minutes in rural locations and longer in very remote locations. One filter tape is sufficient for approximately 700 aerosol collection spots corresponding to one or more months of operation in urban areas, a year or more in rural areas.

The aethalometer converts the result of its filter attenuation measurement into BC mass concentration by a conversion factor of 19.2 m2/g. Aethalometer BC agrees with collocated filter samples analyzed for elemental carbon (Hansen and McMurry, 1990). Applications of the aethalometer include air quality monitoring in urban (Hansen and Novakov, 1989; Hansen and Novakov, 1990) and more remote locations (Rosen et al., 1984; Hansen et al., 1993; Pirogov et al., 1994), transport studies (Parungo et al., 1994), and source characterization.

NO and NOy

Nitric oxide (NO) is continuously measured by the chemiluminescence nitric oxide-ozone method. This method is based on the gas-phase chemical reaction of NO with ozone. In this method ambient air is mixed with a high concentration of ozone so that any NO in the air sample will react and thereby produce light. The light intensity is measured with a photomultiplier and converted into an electronic signal that is proportional to the NO concentration. To measure NOx concentrations, the sum of NO and NO_2 (nitrogen dioxide), the air sample is first reduced to NO, either by a heated catalyst (molybdenum or gold in the presence of CO) or chemically using $FeSO_4$, adding to the NO already present in the sample, then injected into the reaction chamber for measurement as described above. The NO_2 concentration is derived by subtracting the NO from NOx.

The reduction of NO_2 to NO by these methods is not specific, and a number of other nitrogen-containing species are reduced to NO that can interfere with the measurement of NO_2 (e.g., HNO_3, PAN, N_2O_5, HONO, and NO_3). Therefore, the thermal catalytic method is used to measure NO, and then NO plus other nitrogen oxides as a group. If the group is not well defined, it is referred commonly as NOx, since the species included in the group depend on factors such as inlet and line losses and environmental factors. HNO_3 is most prone to line losses. Placing the converter as close to the sample inlet as possible minimizes these losses. Chemiluminescence analyzers that are configured in this manner are commonly known as NOy analyzers. NOy, or reactive nitrogen oxides, consists of a variety of species, the most abundant of which are NO, NO_2, PAN and HNO_3. A TEI 42S NO/NOy analyzer will be used in the mobile van. The instrument has a detection limit of about 0.1 ppb (60 sec averaging time).

Carbon monoxide

The TEI Model 48C carbon analyzer will be used in the mobile sampling. The instrument has a lower detection limit of 0.4 ppm. The analyzer is based on EPA Method EQSA-0486-060.

Automated Gas Chromatography with Mass Spectrometry

The system we propose to use for this project is the unit that is currently being used by DRI in the Central California Ozone Study. The system is based upon a commercial GC/MS

system, a commercial preconcentrator/inlet and a custom-built manifold to introduce the sample from outside the shelter to the inlet. The system consists of a Varian 3800 Gas Chromatograph which is interfaced to an Entech model 7100 automated preconcentrator, a Varian Saturn 2000 Ion Trap Mass Spectrometer, and a windows-based PC to manage the analytical and data acquisition operations.

The inlet system consists of a pump, two Silicosteel canisters and appropriate valves, flow control and electronic controller. This allows a sample to be collected slowly, integrating the sample over 40 minutes (or longer) and then injecting the sample through the preconcentrator. Two canisters are used so that one can be evacuated and cleaned while the other is filling with the next sample. This way the carryover of compounds from one sample to the next is minimized.

A dual column system is used to measure the full range of C_2 to C_{12} hydrocarbons. A conventional non-polar capillary column (such as 60 m DB-1) for analytes above C_4 and a porous layer open tubular (PLOT) column is used for C_2 to C_4 analytes. The Al_2O_3/KCl PLOT column provides excellent separation of these important compounds while not requiring cryogenic starting temperatures. The effluent from this column will be sent to a flame ionization detector (FID). This is because these compounds do not require the confirmation of the mass spectrometer.

The target species include C_2 to C_{12} hydrocarbons, methanol, ethanol, and other alcohols. Also included are C_2 and larger carbonyls including acetone, methyl ethyl ketone (butanone), benzaldehyde and others. MTBE and other oxygenates used in fuels are included as is isobutene, an important breakdown product of MTBE. Oxygenated compounds in surface coatings such as benzaldehyde, benzoic acid, and butylacetate are also included, as are the biogenics isoprene, alpha and beta pinene, and limonene. Commonly detected halocarbons are also included. The detection limits for these species are about 0.2 ppbv for all targeted species.

Canister Sampling System

Stainless steel SUMMA™-polished canisters of 3-L capacity will be used for volatile hydrocarbon (C_2-C_{12}) collection. These canister samples are suitable for analysis of speciated hydrocarbons by EPA Method TO-14, as well as for analyses of CO, CO_2, methane, and oxygenated species. Prior to sampling, the canisters are cleaned by repeated evacuation and pressurization with humidified zero air, and certified as described below. The sampling procedure essentially follows the pressurized sampling method described by EPA Methods TO-12 and TO-14 and the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). A stainless steel Viton pump draws in ambient air from the sampling manifold to fill and pressurize the sample canisters. A flow control device maintains a constant flow into the canisters over the desired sample period. This flow rate is preset to fill the canisters to about 1 atm above ambient pressure at the end of the sampling period (as described by EPA Method TO-14).

Prior to sampling, the canisters are cleaned by repeated evacuation and pressurization with humidified zero air, as described in the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). Six repeatable

cycles of evacuation to ~0.5 mm Hg absolute pressure, followed by pressurization with ultra-high-purity (UHP) humid zero air to ~20 psig were used. The difference between the DRI procedure and the EPA recommended method is that in the DRI method canisters are heated to 140 °C during the vacuum cycle, and more cycles of pressure and vacuum are used. At the end of the cleaning procedure, one canister out of six in a lot is filled with humidified UHP zero air and analyzed by the gas chromatograph/flame ionization detection (GC/FID) method. The canisters are considered clean if the total non-methane organic compound (NMOC) concentration is less than 20 ppbC.

Sampling Method for Heavy Hydrocarbons

Heavy hydrocarbons, defined as hydrocarbons in the range of C_8 to C_{20}, are collected using Tenax-TA (Alltech) solid adsorbent. Prior to use, the Tenax-TA solid adsorbent is cleaned by Soxhlet extraction with hexane/acetone mixture (4/1 v/v) overnight, and dried in a vacuum oven at ~80 °C. The dry Tenax is packed into Pyrex glass tubes (4 mm i.d. x 15 cm long, each tube containing 0.2 g of Tenax) and thermally conditioned for four hours by heating in an oven at 300 ^{o}C under nitrogen purge (25 ml/min nitrogen flow). Approximately 10% of the precleaned Tenax cartridges are tested by GC/FID for purity prior to sampling. After cleaning, the Tenax cartridges are capped tightly using clean Swagelok caps (brass) with graphite/vespel ferrules, placed in metal containers with activated charcoal on the bottom, and kept in a clean environment at room temperature until use. When the exposed cartridges are removed, they are immediately plugged with Swagelok caps, and stored in a can designated for exposed cartridges with activated charcoal on the bottom. The exposed cartridges are stored inside a refrigerator and returned to the laboratory in a cooler.

GC/FID Analysis of C_2-C_{12} Hydrocarbons

Gas chromatography with flame ionization detector is the established technique for monitoring volatile hydrocarbons in ambient air. The DRI analytical procedure for analysis of C_2-C_{12} hydrocarbons is consistent with the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215) and is described below.

The GC/FID response is calibrated in ppbC, using primary calibration standards traceable to the National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM). The NIST SRM 1805 (254 ppb of benzene in nitrogen) is used for calibrating the analytical system for C_2-C_{12} hydrocarbon analysis, whereas 1 ppm propane in a nitrogen standard (Scott Specialty Gases), periodically traced to SRM 1805, is used for calibrating the light hydrocarbon analytical system. Based on the uniform carbon response of the FID to hydrocarbons, the response factors determined from these calibration standards are used to convert area counts into concentration units (ppbC) for every peak in the chromatogram.

4.3 Analysis of Monitoring Data

The ambient fixed location and mobile sampling data will be used to characterize the diurnal variations in relative contributions of gasoline and diesel vehicles to the ambient level of ozone precursors by day of the week. For each sample integration period, the time series of NO

and CO will be related to indicators of compression-ignition exhaust (black carbon and heavy hydrocarbons) and spark-ignition exhaust (MTBE) for the carryover, ozone inhibition, and ozone accumulation periods by day of the week. From the NO, CO, BC, MTBE, and nC_{10}-nC_{15}, we will estimate the fractional contributions of spark-ignition and compression-ignition emissions of NO, and NMHC as described as described below.

First, we will use [BC]/[MTBE] ratios to estimate the ratio of vehicle miles traveled by compression-ignition vehicles to spark-ignition vehicles (VMTci/VMTsi) using the following equation.

$$\frac{[BC]}{[MTBE]} = \frac{BCci}{MTBEsi} \text{ x } \frac{VMTci}{VMTsi}$$

where
[*BC*] = measured black carbon concentration in µg/m^3,
[*MTBE*] = measured MTBE concentrations in µg/m^3,
BCci = assumed average CI emission rate of black carbon in grams/mile, and
MTBEsi = assumed average SI emission rate of MTBE in grams/mile.

$$\text{The ratio of VMT, } A = \frac{VMTci}{VMTsi} = \frac{[BC]}{[MTBE]} \text{ x } \frac{MTBEsi}{BCci}$$

The ratio of the CI and SI source contribution estimates (SCE) to NO can be estimated from *A* and assumed average NO emission rates for CI and SI as follows.

$$\frac{NOsceci}{NOscesi} = \frac{NOci}{NOsi} \text{ x } A$$

It must be recognized that while compression-ignition vehicles are a major source of black carbon, they are not the sole source. Accordingly the results of this method would yield an upper limit for the contribution of CI exhaust.

Ratios of the CI and SI source contribution estimates to NMHC and CO can be estimated in much the same way.

The ratio of VMT due to CI and VMT due to SI, *A*, can also be estimated from [CO] and [NO].

[*CO*] is proportional to *COci* x *VMTci* + *COsi* x *VMTsi* and

[*NO*] is proportional to *NOci* x *VMTci* + *NOsi* x *VMT si*

where

[*CO*] = measured carbon monoxide concentration in µg/m^3,
[*NO*] = measured nitric oxide concentrations in µg/m^3,
COci and *COsi* = assumed average CI and SI emission rates of CO in grams/mile, and

NOci and *NOsi* = assumed average CI and SI emission rates of NO in grams/mile.

A is determined from the following equation.

$$\frac{[CO]}{[NO]} = \frac{COciA + COsi}{NOciA + NOsi}$$

The three approaches described above will be compared with the results of the source attributions derived from the Chemical Mass Balance (CMB) receptor modeling described in the next section.

4.4 Source Composition Profiles and Source Attribution

The CMB receptor model consists of a least-squares solution to a set of linear equations, which expresses each receptor concentration of a chemical species as a linear sum of products of source profile species and source contributions. The source profile species (the fractional amount of the species in the VOC emissions from each source type) and the receptor concentrations, each with uncertainty estimates, serve as input data to the CMB model. The output consists of the contributions for each source type to the total ambient VOC as well as to individual VOC species concentrations. The model calculates values for contributions from each source and the uncertainties of those values. Input data uncertainties are used both to weight the relative importance of the input data to the model solution and to estimate uncertainties of the source contributions.

The emissions inventory is the starting point for a CMB source apportionment to identify potential contributors to ambient concentrations. Vehicle-related emissions, including exhaust, evaporated fuel, and even liquid fuels are ubiquitous in all urban areas and are always included. Architectural (i.e., paints) and industrial solvents (i.e., cleaning and process solvents, as in printing) are also common to, but highly variable in, most urban areas. Petrochemical production and oil refining are more specific to certain urban areas where these facilities exist. Biogenic emissions are larger in the eastern U.S., where forests are lush, in contrast to the arid west.

The source composition profiles that are used in receptor modeling and as input to photochemical air quality models should be current and regionally specific in order to account for temporal and regional variations in fuel formulations and distribution of area and point sources. The major sources for which updated profiles need to be considered for this project are emissions from regional background, motor vehicle exhaust, gasoline liquid and headspace, surface coatings, commercial natural gas, liquefied petroleum gas, and industrial facilities. The source samples that are proposed for this project are described in this section along with currently available profiles that may be applicable for this project.

Regional Background and Biogenic Emissions. Regional upwind, background VOC compositions will be derived from ambient samples collected at Catalina Island and San Nicolas Island during the 1997 Southern California Ozone Study (SCOS97-NARSTO). These samples typically contain higher abundances of relatively nonreactive hydrocarbons such as ethane and propane and oxidized species, primarily aldehydes.

Vehicle Exhaust. In urban locations, motor vehicle exhaust and evaporative emissions of gasoline are major sources of hydrocarbon emissions. Composites of dynamometer measurements of vehicles of varying age and mileage or on-road measurements (e.g., tunnels and roadways) are commonly used to represent fleet-averaged exhaust profiles. Profiles based on dynamometer tests should include a weighted sum of exhaust profiles for noncatalyst vehicles, high-emitting vehicles and catalyst-equipped vehicles with site-specific weighting factors to approximate the fleet-averaged exhaust composition. The fuels used in the dynamometer tests should resemble the fuels used in the study region at the time the ambient samples are collected. On-road measurements are usually preferred in CMB applications because they include a composite of the exhaust from many vehicles, which more closely represents the local vehicle population than dynamometer tests of a small sample of vehicles. However, tunnel measurements also include varying amounts of diesel exhaust and running evaporative losses.

Diesel and gasoline exhaust profiles are similar with respect to the composition of light hydrocarbons, and are often collinear in CMB calculations. Ethene, acetylene, 1-butene, iso-butene, propane, propene, isopentane, n-pentane, 2,2-dimethylbutane, 2-methylpentane, n-hexane, benzene, 3-methyhexane, toluene, ethylbenzene, m- & p-xylene, m-ethyltoluene, and 1,2,4-trimethylbenzene, are the most abundant compounds in either or both of these emissions. Several of these are short-lived, and are only used in CMB calculations where fresh emissions are expected. Major differences between these two exhaust profiles are evident for: 1) acetylene, iso-butene, isopentane, n-hexane, and 2-methylhexane, which are most abundant in gasoline exhaust; and 2) propene, propane, 2,2-dimethylbutane, n-decane, and n-undecane which are more abundant in diesel exhaust. Previous studies showed that source attributions between tailpipe and evaporative emissions from receptor modeling can vary greatly depending on the particular profile chosen for tailpipe emissions (Harley et al., 1992; and Fujita et al., 1994). This is because tailpipe emissions are a mixture of hydrocarbons produced during combustion (e.g., acetylene, ethene, propene, and benzene) along with unburned gasoline resulting from incomplete combustion. The relative abundances of combustion by-products in the exhaust profile vary with emission control technology, level of vehicle maintenance and operating mode. In the CMB calculation, liquid gasoline represents the additional unburned gasoline (due to misfiring and other engine malfunctions) that is not included in the exhaust profile, plus evaporative emissions from gasoline spillage, hot soaks, and some portion of resting losses (leaks, permeation). The profile for gasoline headspace vapor is taken to represent fuel tank vapor losses (e.g., migration of fuel vapor from the canister).

The reformulation of gasoline has significantly affected the composition of motor-vehicle related emissions in recent years. Both the federal government and the State of California have developed specifications for reformulated gasoline (RFG). The federal program is required for all severe and extreme ozone nonattainment areas, whereas the California program applies throughout the state. Both California and federal RFGs were introduced in two phases. California Phase 1 was introduced in 1992 and Phase 2 was introduction in 1996. Phase I of the federal program was introduced in 1995 and Phase II is scheduled for 2000.

The California Phase 2 RFG specifications apply to all gasoline sold in California beginning January 1, 1996, and include a maximum 80 ppmw sulfur content (average of 30 ppmw), a maximum 1.2% benzene content by volume (average of 0.8), a maximum 10.0% olefin content, a maximum 2.7% oxygen content by volume, a maximum T90 and T50 of 330 °F and

220 °F, respectively, maximum 30% aromatic hydrocarbon content by volume (average of 20%), and a maximum RVP of 7.0 psi. Investigations of the effects of RFG on automotive emissions have been conducted through the Auto/Oil Air Quality Improvement Research Program (AQIRP), by EPA, ARB, and individual oil companies. Results of the Auto/Oil AQIRP are illustrative of the general response of automotive emissions to changes in fuel parameters.

Compositional differences of vehicle exhaust from Transitional Low Emission Vehicles (TLEVs) operating on conventional industry-average gasoline (RF-A) versus California Phase 2 RFG were summarized by the California Air Resources Board (1993). The summary includes data from testing programs conducted by the ARB, the Auto/Oil AQIRP, and Chevron Research & Technology Company. The motor vehicle test data were renormalized in terms of weight fractions, and the weight fractions for each species for all tests on an individual vehicle were averaged. The composite profiles for each vehicle were averaged to create composite profiles for each fuel. Separate composite profiles were calculated for each bag of the U.S. EPA 1975 Federal Test Procedure (FTP). For the composite FTP, the average weight fraction of n-alkanes decreased from 15.3% with RF-A to 8.5% with RFG, while the branched alkanes increased from 24.5% with RF-A to 35.8% with RFG. The relative abundances of cycloalkanes and alkynes remained unchanged, while olefins and oxygenates showed slight increases with RFG. Emissions of aromatic compounds decreased from 35.2% with RF-A to 27.7% with RFG. Differences are higher for specific compounds (e.g., benzene and MTBE). These compounds or their ratios serve as useful tracers for RFG.

Gasoline Liquid and Vapor. Running and resting losses are the two sources of evaporative loss from vehicles travelling on the road. Running losses are releases of gasoline vapor from the fuel system during vehicle operation as a result of the heating of the fuel tank. Vapors are released when the rate of fuel vapor formation exceeds the capacity of the vapor storage and purge systems. The composition of running losses tend to resemble headspace vapors if the canister is saturated, and butane-enriched vapors if the canister is not saturated. The canister similarly affects the composition of diurnal evaporative emissions. Resting loss evaporative emissions are due to migration of fuel vapors from the evaporative canister, from leaks, and from fuel permeation through joints, seals, and polymeric components of the fuel system. Most of these losses tend to appear more like whole liquid gasoline. Hot soaks also resemble liquid gasoline.

Liquid gasoline contains many compounds in common with gasoline-vehicle exhaust. It is depleted in products of combustion such as ethane, ethene, acetylene, propene, and to some extent, benzene. Evaporated gasoline is also depleted in these combustion compounds, as well as heavier hydrocarbons that volatilize more slowly from liquid fuels. Isobutane, n-butane, t-2 butene, and especially isopentane are enriched in evaporated gasoline. MTBE and its thermal decomposition product, isobutylene, stand out as a large constituent of gasoline exhaust emissions that clearly separates these from diesel in areas where it is used as an additive. These differences are sufficient for CMB separation of gasoline exhaust from liquid and evaporated gasoline in ambient air, and from diesel exhaust.

Commercial Natural Gas and Liquefied Petroleum Gas. The commercial natural gas (CNG) profile is based on samples taken in the summer of 1972 at Los Angeles, CA and in the summer of 1973 at El Monte, CA (Mayrsohn et al., 1976, 1977). The geogenic natural gas

(GNG) profile is based upon samples taken in the spring of 1972 in Newhall, CA and at a well head in Redondo Beach, CA in the fall of 1973. The composition of the samples of both types of natural gas did not vary despite the differences in time and location of sample collection (Fujita et al., 1994b).

Surface Coatings. Although solvents from paints and industrial uses are large components of all ROG inventories, their reported profiles are few (Guo et al., 1998; Kitto et al., 1997). The most recent data are those of Censullo et al., (1996). Eleven categories of coatings were analyzed in this study. In all detailed species profiles were obtained for 106 samples of water-based and solvent-based coating samples. Surface coating profiles for solvent-based industrial maintenance coatings, solvent-based medium gloss/high gloss, solvent-based primers and sealers, quick dry primers and enamels, and thinning solvent were applied in the apportionments. These are largely depleted in the species common to fuel use and production, with larger abundances of styrene, n-decane, and especially "other" compounds. The "other" VOCs are quantified and differ substantially among the different coatings tested. Most of these other compounds are oxygenated compounds that are not measured in PAMS. California and other states require special solvent and coating formulations to comply with air quality emissions requirements. Coating and solvent profiles are likely to be very specific to a particular area.

In addition to the relative contributions of on-road gasoline and diesel vehicles, the detailed speciation of VOC from the mobile sampling and the time-resolved VOC speciation at Los Angeles, Azusa, and Pico Rivera monitoring stations will also allow for source attribution of other sources of VOC by time of day and day of the week. These analyses will address questions regarding the source contributions of VOC carried over from the previous evening and the relative importance of on-road versus other area sources in the diurnal variations in VOC/NOx ratios. Diurnal variations in VOC composition will be used to determine day-of-the-week differences in ozone formation potential and reactivity of the VOC mix.

4.5 Evaluation of Alternative Hypotheses

It is expected that the Phase II measurements will capture the day-of-the-week differences in traffic characteristics and in the emissions of NOx and VOC and the associated VOC/NOx ratios. We will examine the data to investigate the effect of surface and aloft carryover of VOC and NOx and their effect on surface VOC and NOx concentrations during the ozone inhibition and accumulation periods. It must be recognized that the latter effects are influenced by the prevailing meteorology during the field study and may not be representative of the seasonal average. These factors will be addressed in Phase III utilizing supplemental data sources, which include historic SCAQMD monitoring data, recent PAMS hydrocarbon data, and relevant data from recent field studies such as the 1997 Southern California Ozone Study (SCOS-NARSTO) and the Central California Ozone Study (CCOS).

The investigation of the possible changes in photolysis rates on the WE effect will be performed by analyzing an existing data set of UV actinic flux collected near a freeway at Sunol, CA during the summer 2000 Central California Ozone Study (CCOS). The photolysis of nitrogen dioxide, ozone, formaldehyde and other carbonyl containing compounds are the initial steps in the production of photochemical air pollutants. The photolysis rate of an air pollutant is the product of the compound's mixing ratio and its photolytic rate parameter. The photolytic rate

parameter is the integral over all wavelengths of the product of the compound's absorption cross-section, quantum yield and actinic flux. The actinic flux was measured with a diode array spectrometer that has a hemispheric sampling head (2π response). The data record extends for a period of over two months. Therefore, it will be possible to make some reasonably valid weekend to weekday comparisons of the actinic flux according to wavelength and, hence, photolysis rates of key reactive species. Correlations of the actinic flux with concurrent data for O_3, black carbon, and particulate nitrate will be examined.

Table 4-1
Measurements at Fixed Sites During Field Study

Site	South Coast AQMD					DRI	Others
	O3	NO/NOx	CO	PM10 mass	PAMS		
Hawthorne	x	x	x		canister/GC-FID		
North Long Beach	x	x	x	TEOM			
Lynwood	x	x	x				
Anaheim-Harbor Blvd	x	x	x	BAM			
Burbank-W Palm Avenue	x	x	x	TEOM	auto GC-FID, DNPH		PAN (DGA)
Los Angeles-North Main	x	x	x	BAM	canister/GC-FID (ARB)	Aethalometer	
Pasadena-S Wilson Avenue	x	x	x				
La Habra	x	x	x				
Pico Rivera	x	x	x		auto GC-FID, DNPH		
Azusa	x	x	x	BAM	canister/GC-FID	Auto GC/MS, Aethalometer	PAN (DGA), NOy (CE-CERT)
Pomona	x	x	x				
Upland	x	x		TEOM	canister/GC-FID		
Riverside-Rubidoux	x	x	x	BAM, TEOM			